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Properties of Distillers Grains Composites: A Preliminary Investigation

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Abstract Interest in renewable biofuel sources has intensified in recent years, leading to greatly increased production of ethanol and its primary coproduct, Distillers Dried Grain with Solubles (DDGS). Consequently, the development of new outlets for DDGS has become crucial to maintaining the economic viability of the industry. In light of these developments, this preliminary study aimed to determine the suitability of DDGS for use as a biofiller in low-cost composites that could be produced by rapid prototyping applications. The effects of DDGS content, particle size, curing temperature, and compression on resulting properties, such as flexural strength, modulus of elasticity, water activity, and color were evaluated for two adhesive bases. The composites formed with phenolic resin glue were found to be greatly superior to glue in terms of mechanical strength and durability: resin-based composites had maximum fiber stresses of 150–380 kPa, while glue composites had values between 6 kPa and 35 kPa; additionally, glue composites experienced relatively rapid microbial growth. In the resin composites, both decreased particle size and increased compression resulted in increased mechanical strength, while a moderate DDGS content was found to increase flexural strength but decrease Young's modulus. These results indicate that DDGS has the potential to be used in resin glue-based composites to both improve flexural strength and improve potential biodegradability.

Keywords Biofillers · Bioplastics · Composites · Mechanical properties · Physical properties · Testing

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Introduction

In recent years, interest in renewable energy sources has led to explosive growth in the biofuels industry. While biological waste materials such as residue straw, corn stover, perennial grasses, and legumes can be used, corn starch is by far the most common substrate used for ethanol manufacture because of its economic viability [1]. In fact, corn ethanol production has nearly tripled since 2000, and has recently been growing at a rate between 15% and 20% per year.

During processing, along with the main product, ethanol, two coproducts are generated: Distillers Dried Grain with Solubles (DDGS) and carbon dioxide. A rough rule is that for every 1 kg of corn utilized, 1/3 kg of each of the products, that is ethanol, DDGS, and CO_2, will be generated. DDGS is composed of the nonfermentable components of the original grain, namely protein, lipids, and fiber. In 2005, approximately 8.5 million metric tons of DDGS were produced from this industry; nearly 10 million metric tons were produced at the end of 2006. Even if the ethanol industry continues to expand at a comparatively modest growth rate of 10–15% per year, between 35 and 70 million metric tons of DDGS could be produced per year by 2020.

At present, the only large-scale use for DDGS is as a livestock feed. It has a high protein content, which makes it attractive to livestock producers. However, with an ever-

increasing supply of distillers grains, market saturation must be avoided in order to maintain the economic viability of the ethanol industry. It is therefore clear that alternate paths to utilize this coproduct must be developed. Several potential alternatives have been proposed, including bioplastics [2] and human food additives [3].

But to date, very little research has been reported that pursue these avenues. Fillers are often used in industrial applications in the hopes of creating stronger (or at least almost equivalent) products at a lower cost [4]. In this capacity biomaterials are well-suited because they are inexpensive, and in some cases can increase the mechanical strength of the finished product. Only two published studies thus far have investigated using DDGS as a filler in plastic/fiber composites. Among other materials [5], studied the effect that inclusion of DDGS had on the strength of injection-molded polypropylene and polyethylene blends. They found flexural strength values in the range of 20–40 MPa and modulus of elasticity in the range of 400–1100 MPa. These were, unfortunately, approximately 10–20% lower than control values. Nonetheless, these results indicate that with further modifications, it may be possible to use DDGS as a viable filler for injection-molded composite applications. Using phenolic resin [6] studied the effect of using DDGS as a filler for compression-molded blends. They found that DDGS inclusion levels between 25% and 50% resulted in adequate mechanical strength compared to the phenolic resin baseline, even though strength decreased as DDGS level increased.

Even so, extrusion, injection molding, or compression molding of plastics are not always the most cost-effective methods of manufacture for biomaterials [7]. In light of this, we chose to study the use of relatively inexpensive adhesives and small-scale fabrication methods to determine if these could be used to develop viable production systems. In this article we aim to lay ground work for another industrial application: DDGS/adhesive composites using rapid prototyping applications.

Experimental

DDGS was obtained from a commercial fuel ethanol plant during May 2006, and was stored in sealed plastic buckets at room temperature (23 ± 1 °C) until use. Using standard AOAC methods, it was determined that the DDGS had, on a dry basis (Table 1), a protein content of 27.6%, fiber content of 11.1%, fat content of 9.3%, ash content of 4.2%, and other carbohydrates of 47.8%. Approximately half of the sample was left as-received, while the remainder was ground in a laboratory mill (C/11/1, GlenMills Inc., Clifton, NJ) to reduce mean particle diameter from 0.700 mm to 0.343 mm. Particle size was determined according to standard method S319.3 [8]. Two adhesives were then used to produce composites: phenolic resin glue (DAP Weldwood Plastic Resin Glue, Baltimore, MD—which has a urea-formaldehyde base) and wood glue (Elmer's Interior Carpenter's Wood Glue, Columbus, OH).

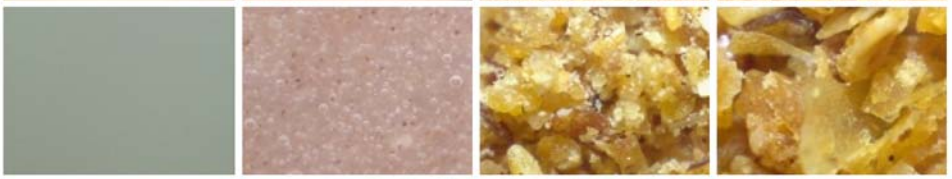
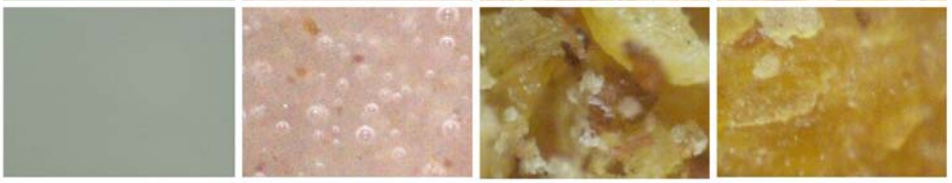
Composite Preparation

A completely randomized design was used with two levels for each of five independent variables: compression (0 kPa and 25.0 kPa), DDGS inclusion (25% and 50%), heat treatment (23 °C and 75 °C), particle size (0.343 mm and 0.700 mm), and type of adhesive (phenolic resin glue and wood glue). Each treatment condition was formed once (i.e., $n = 1$) for this 2^5 full factorial design (Table 2), which thus resulted in 32 total treatment combinations (i.e., experimental units). Additionally, one resin glue sample was formed at 0% DDGS, 23 °C, and 0 kPa compression to serve as a control (Table 1) for each type of adhesive, for comparison purposes.

The adhesives and DDGS were combined such that the total mass of composites to be formed was 30.00 g (i.e., for the 25% DDGS composites, 7.5 g of DDGS was added to 22.5 g of adhesive, but for the 50% DDGS composites, 15.0 g of DDGS was added to 15.0 g of adhesive), while the mass of composites to be left uncompressed was 25.00 g (i.e., for the 25% DDGS composites, 6.25 g was added to 18.75 g of adhesive, but for the 50% DDGS composites, 12.5 g of DDGS was added to 12.5 g of adhesive). The adhesives and DDGS were thoroughly mixed by hand, using a consistent method. Once combined, the samples were placed in 50 × 15 mm Petri dishes (Falcon 351007, Becton Dickinson Labware, Franklin Lakes, NJ), compressed, using a consistent method, to remove air pockets, and covered. At this time, 5 kg weights, giving a compression of 25.0 kPa, were placed on the samples to be compressed. Samples to be subjected to heat treatment were placed in a 75 ± 1 °C oven for 5 h; all other samples were left on the bench top at ambient conditions (23 ± 1 °C, 44 ± 9% relative humidity). Samples from the oven were placed on the bench following the heat treatment. These experimental procedures were implemented in order to simulate some of the processing conditions that may occur during rapid prototyping applications, where the level of adhesive is often greater than the level of filler material.

The samples which were compressed were subjected to this treatment for 72 h, after which the lids and compression weights were removed, and the samples remained on the bench top for another 24 h to cure. At this time, the composites were transferred to desiccators at 23 ± 1 °C and 14 ± 1% relative humidity. At 7 d after formation, the

Table 1 Chemical and physical properties of raw base materials used for the biocomposite study

Property	Adhesive		Particle Size	
	Glue	Resin	0.343 mm	0.700 mm
Moisture Content (% db)	30.55	37.50	8.23	
Chemical Properties				
Protein (% db)	-	-	27.60	
Fiber (% db)	-	-	11.10	
Other carbohydrates (% db)	-	-	47.80	
Fat (% db)	-	-	9.30	
Ash (% db)	-	-	4.20	
Total			100.00	
Physical Properties				
Color				
L (-)	87.18	35.40	48.00	44.89
a (-)	-1.03	11.05	8.74	10.83
b (-)	25.21	14.49	22.59	22.50
Water Activity (-)	1.000	0.952	0.446	0.453
Magnification				
10x				
60x				
200x				

samples were removed from the desiccators and were tested for physical and mechanical properties.

Testing

From the large battery of potential tests that exist for determining the suitability of composites [7], we chose three to encapsulate the fitness of our samples: 3-point bending strength, color, and water activity. The strength of each composite was measured with an Instron compression tester (Model 5564, Instron Corporation, Canton, MA), using a 1 kN load cell. ASTM Method D790 [9] was used, with a sample diameter-to-thickness ratio of approximately 5:1. During testing, a sample was placed on the lower fixture, and the upper fixture was lowered at a constant rate of 0.1 in/min (2.54 mm/min). Applied force was measured, as was travel distance; thus stress and strain were determined via the compression tester's computer control software. Captured data were analyzed and bending strength was determined for each sample. Color was measured using a spectrocolorimeter (LabScan XE, Hunter Associates Laboratory, Reston, VA) using the L–a–b opposable color scales, where L quantified the brightness/darkness, a quantified redness/greenness, and b quantified yellowness/blueness of the samples [10]. Water activity was measured using a calibrated water activity meter (AW Sprint TH 500, Novasina, Talstrasse, Switzerland).

Additionally, digital images at 10, 60, and 200× magnification were captured using a computer-controlled microscope (Digital Blue Microscope QX5, Prime Entertainment Inc., Marietta, GA).

Table 2 Experimental design used to study the effects of adhesive used, DDGS inclusion, processing temperature, compression pressure, and particle size on resulting composite properties

Treatment	Adhesive	DDGS Level (%)	Temperature (°C)	Compression (kPa)	Particle size (mm)
1	Wood Glue	25	23	0	0.343
2					0.700
3				25	0.343
4					0.700
5			75	0	0.343
6					0.700
7				25	0.343
8					0.700
9		50	23	0	0.343
10					0.700
11				25	0.343
12					0.700
13			75	0	0.343
14					0.700
15				25	0.343
16					0.700
17	Resin Glue	25	23	0	0.343
18					0.700
19				25	0.343
20					0.700
21			75	0	0.343
22					0.700
23				25	0.343
24					0.700
25		50	23	0	0.343
26					0.700
27				25	0.343
28					0.700
29			75	0	0.343
30					0.700
31				25	0.343
32					0.700

Statistical Analysis

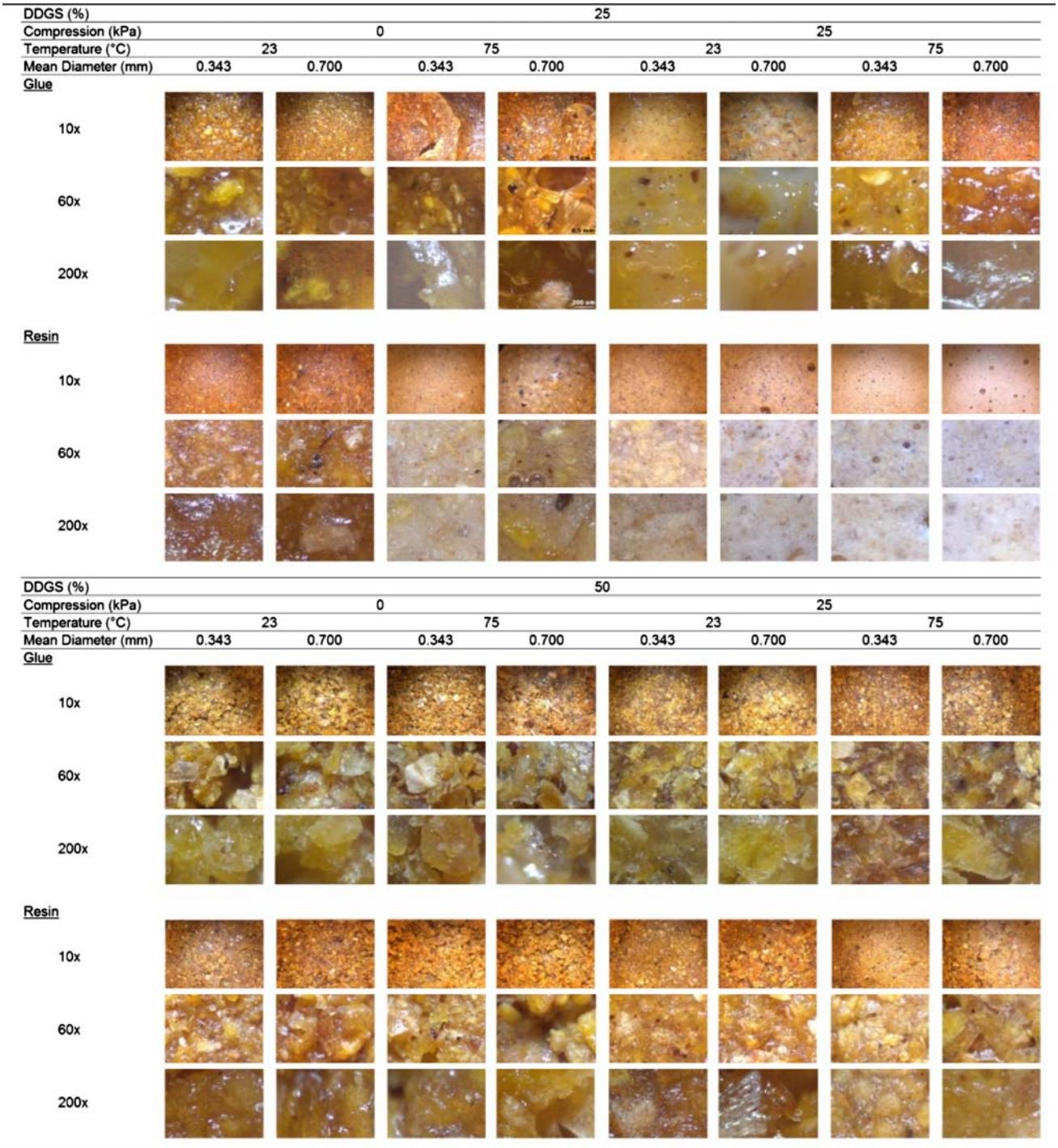
The collected data were analyzed by general linear models using the Proc GLM procedure to determine the main effects and least significant differences (LSD) using SAS V.8 (SAS Institute, Cary, NC), with a Type I error rate (α) of 0.05.

Results and Discussion

Unfortunately, the glue-based composites with 25% DDGS failed to form; the uppermost few millimeters case-hardened and formed a seal which prevented further moisture loss, which left the lower fraction wet—and thus the composites could not cure. The crust did not develop quickly for those composites which were not heat-treated, and the entire sample remained wet for several days following preparation. This issue prevented testing for both mechanical strength and water activity on all 25% DDGS/glue composites. None of the resin glue-based composites experienced this problem and appeared to cure consistently.

Under magnification (Table 3), it became apparent that the 50% DDGS composites did not form as well as those at the 25% level; the surface texture of the samples with less DDGS was much smoother with fewer fissures. It appeared that the adhesive was absorbed by the DDGS to some extent and could not form a uniform matrix in the higher DDGS content samples. Compression alleviated this

Table 3 Visualization of treatment combination effects due to adhesive used, DDGS inclusion, processing temperature, compression, and particle size on resulting composites



problem somewhat in the 50% DDGS samples, although voids were still present. Additionally, decreased particle size aided the formation of a more tightly bound matrix, with fewer cavities in higher DDGS content composites. In the 25% DDGS/resin glue samples, the hollow spaces appeared to be not from a mechanical failure in the matrix, but from air pockets that could not escape during the curing process. Temperature did not, however, appear to have an impact on surface texture. The images suggested that compressed high-resin glue samples formed the most uniformly tightly bound composites, and would therefore be the most sound. Aesthetically, a lower DDGS content

composite would be better suited to those applications necessitating a smooth, even surface.

Some shrinkage during curing was observed in all uncompressed samples, as well as in several ground, compressed samples. This issue should be further studied in the development of a production protocol.

The onset of deterioration in the wood glue samples was swift (using visual observation for the presence of mold development); the first composite began to mold 10 d following preparation. Within 30 d, every wood glue composite which had not been heat treated exhibited mold growth. By 45 d, half of the heat treated samples showed signs of spoilage as well. However, none of the resin glue composites experienced this problem. A likely explanation for the lack of spoilage in the resin glue samples was the presence of formaldehyde, which can effectively kill many of the organisms responsible for decomposition. The glue samples which did not spoil had the lowest water activity values; thus water activity appears to be a primary factor affecting decomposition. The addition of preservatives, or a drying step, during manufacturing would be essential were this type of adhesive to be used in production, unless a low water activity could consistently be achieved by other means.

Mechanical Strength

For polymer and composite applications when biofillers are added, a primary goal is to either improve, or at least not drastically decrease, material strength and stiffness [7]. Unfortunately, one of the challenges in utilizing biological materials for composites is that of achieving appropriate compatibility between the filler and the adhesive or plastic [11]. Moreover, many studies have found that mechanical strength decreases as filler level increases [12–14]. Although not specifically tested, it appeared to be the case in this study as well. Resin glue composites yielded at a substantially greater maximum fiber stress and had a higher Modulus of Elasticity than their glue-based counterparts. The largest stress recorded was 381 kPa, observed for the room temperature, compressed, ground, 25% DDGS/resin glue composite, while the lowest was 6 kPa, observed for the room temperature, uncompressed, ground, 50% DDGS/glue composite (Table 5). The average stress and Modulus of Elasticity of the DDGS/resin glue samples were 241 kPa and 726 kPa, respectively, while the wood glue yielded at only 19 kPa stress and had a Modulus of Elasticity of 34 kPa (Tables 4 and 5). These trends indicated that plastic resins generated far stronger composites than their wood glue equivalents. While these values were considerably lower than those obtained by [5], who used injection molding, the methods of production required less equipment and energy, and thus may be more cost-effective, depending on final potential applications, such as rapid prototyping.

As with other studies, the amount of DDGS incorporated affected the resulting mechanical strength of the composites [5, 6]. The glue trials with 25% DDGS failed to cure, making them completely unsuitable for analysis. However, the addition of a moderate amount of DDGS appeared to be beneficial to the allowable stress in the resin glue composites. The resin glue control (i.e., 0% DDGS) had a maximum stress of 242.42 kPa; this was 27.92 kPa lower than the stress for the resin glue composites using 25% DDGS that were also uncompressed and not heat treated; it was, however, 88.46 kPa greater than the uncompressed, non-heat treated, 50% DDGS composite. The Modulus of Elasticity decreased when compared to the same group of composites: the control had an Modulus of Elasticity of 1250.85 kPa, the 25% DDGS, non-heat treated, uncompressed composite had a Modulus of Elasticity of 784.82 kPa (a 37.3% reduction), while the 50% DDGS composite had a Modulus of Elasticity of 433.19 kPa (a 65.4% reduction). Over all resin glue treatments, there was a 22.6% increase (of 49.24 kPa) in the maximum stress when DDGS content was reduced from 50% to 25%, and a 292.54 kPa, or 49.7%, increase in Modulus of Elasticity. These results indicated that there was an optimal percentage of DDGS between 0% and 50% which could increase allowable stress, and thus the DDGS was fulfilling the anticipated role as a filler. Thus the addition of DDGS to resin glue could result in stronger composites with less stiffness; further research should determine exactly what the optimal percentage is. On the other hand, it appears that a high DDGS content is essential for any glue-based product if a composite is to be formed at all.

Compression also resulted in overall increased stress and Modulus of Elasticity, although the difference was not so marked as with the type of adhesive. Over all composites, the average stress of the compressed samples was 177.58 kPa, a 28.26 kPa increase over their uncompressed counterparts. The average Modulus of Elasticity also increased 33.85 kPa, from 468.33 kPa to 502.18 kPa, as compression was added. However, because the average values calculated using both adhesives were dominated by the resin glue values, within each adhesive category, the same trend did not necessarily prevail (Table 4). While compression increased the average resin glue stress by 54.21 kPa, or 25.5%, it decreased the average glue stress by 5.79 kPa, or 25.6%. The average resin glue Modulus of Elasticity increased 12.7%, or 86.41 kPa, while the corresponding wood glue value dropped by 41.1%, or 1838 kPa. A likely explanation is that the wood glue composites failed to cure properly under compression, and that although the surface hardened, the interior was still

Table 4 Main effects due to adhesive used, DDGS inclusion, processing temperature, compression, and particle size on resulting composite properties[a]

Overall	Adhesive				DDGS (%)				Temperature (°C)				Compression (kPa)				Mean diameter (mm)			
	Glue		Resin		25		50		23		75		0		25		0.343		0.700	
Physical property	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Max fiber stress (kPa)	19.38 A	17.66	241.38 B	86.77	267.45 A	67.56	118.80 B	123.35	177.79	137.68	153.17	124.21	149.32	99.60	177.58	151.58	191.43	143.11	174.46	100.87
Modulus of elasticity (kPa)	34.47 A	36.97	725.90 B	284.94	880.77 A	242.87	311.35 B	335.59	433.48	331.84	532.05	468.16	468.33	348.92	502.18	462.16	534.59	423.34	579.18	385.88
Color L (–)	39.68 A	9.77	49.10 B	13.52	46.18	16.91	42.61	5.74	43.10	9.33	45.68	15.33	39.64 A	9.21	49.14 B	13.88	43.49	12.64	44.93	13.88
Color a (–)	7.79	1.29	7.89	1.68	7.10 A	1.51	8.57 B	1.02	8.02	1.27	7.66	1.67	8.55 A	1.30	7.13 B	1.31	7.50	1.36	7.80	1.62
Color b (–)	15.75	4.74	16.45	2.57	14.05 A	4.12	18.14 B	1.86	16.81	2.95	15.38	4.42	15.75	3.88	16.45	3.74	15.85	3.75	15.62	4.56
Water activity (–)	0.77	0.14	0.84	0.07	0.89 A	0.03	0.78 B	0.10	0.86 A	0.04	0.77 B	0.13	0.77 A	0.12	0.86 B	0.04	0.82	0.10	0.82	0.10

Glue	DDGS (%)				Temperature (°C)				Compression (kPa)				Mean diameter (mm)			
	25		50		23		75		0		25		0.343		0.700	
Physical property	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Max fiber stress (kPa)	–	–	19.38	17.66	10.62	3.35	26.39	21.84	22.60	23.88	16.81	13.31	13.98	7.58	29.63	21.67
Modulus of elasticity (kPa)	–	–	34.47	36.97	14.69	7.71	50.29	44.56	44.68	52.89	26.30	21.18	24.20	15.38	53.35	48.96
Color L (–)	36.26	13.12	43.11	2.42	44.97 A	1.38	41.25 B	1.59	42.22	2.40	43.99	2.42	42.65	1.85	43.57	3.12
Color a (–)	7.26	1.31	8.32	1.10	8.10	0.82	8.54	1.42	9.03	0.97	7.61	0.73	7.94	1.45	8.70	0.57
Color b (–)	13.10 A	5.45	18.40 B	1.54	19.52 A	0.78	17.27 B	1.23	18.73	1.40	18.06	1.81	18.09	1.51	18.71	1.72
Water activity (–)	–	–	0.77	0.14	0.85	0.01	0.69	0.16	0.69	0.17	0.84	0.02	0.77	0.14	0.77	0.15

Resin	DDGS (%)				Temperature (°C)				Compression (kPa)				Mean diameter (mm)			
	25		50		23		75		0		25		0.343		0.700	
Physical property	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Max fiber stress (kPa)	267.45	67.56	218.21	98.91	261.38	76.33	223.60	95.94	212.68 A	39.75	266.89 B	110.09	280.15	71.91	232.78	43.74
Modulus of elasticity (kPa)	880.77 A	242.87	588.23 B	255.85	642.88 A	150.62	799.69 B	359.88	680.15	190.45	766.56	355.94	789.78	241.33	752.75	215.81
Color L (–)	56.09 A	14.70	42.11 B	8.01	41.22 A	9.66	56.98 B	12.52	43.13	10.18	55.07	14.37	47.94	14.01	50.26	13.87
Color a (–)	6.95 A	1.77	8.83 B	0.93	8.22	1.38	7.55	1.96	8.86 A	1.00	6.92 B	1.70	7.62	1.40	8.15	1.98
Color b (–)	15.01 A	2.14	17.89 B	2.21	15.20	1.57	17.70	2.85	16.73	2.34	16.16	2.92	16.38	2.16	16.52	3.08
Water activity (–)	0.89 A	0.03	0.79 B	0.06	0.87	0.05	0.81	0.09	0.81	0.08	0.87	0.05	0.84	0.07	0.84	0.08

[a] Means with differing letters for a given property are significantly different ($p < 0.05$) for a given independent variable

Table 5 Treatment combination effects due to adhesive used, DDGS inclusion, processing temperature, compression, and particle size on resulting composite properties

DDGS (%)	0	25								50							
Compression (kPa)	0	0				25				0				25			
Temperature (°C)	23	23		75		23		75		23		75		23		75	
Mean diameter (mm)	–	0.343	0.700	0.343	0.700	0.343	0.700	0.343	0.700	0.343	0.700	0.343	0.700	0.343	0.700	0.343	0.700
Glue																	
Max fiber stress (kPa)	–	–	–	–	–	–	–	–	–	6.00	11.45	14.96	57.98	11.03	14.00	23.92	35.09
Modulus of elasticity (kPa)	–	–	–	–	–	–	–	–	–	6.27	11.10	40.68	120.66	17.31	24.06	32.54	57.57
Color L (–)	–	31.14	34.73	26.25	28.25	56.22	57.93	28.04	27.53	44.11	44.36	40.91	39.51	44.38	47.03	41.20	43.36
Color a (–)	–	8.10	9.48	5.45	6.80	6.00	6.53	7.73	7.97	7.70	9.15	10.04	9.22	7.26	8.28	6.75	8.14
Color b (–)	–	11.92	15.42	7.13	8.72	20.94	21.05	10.22	9.41	19.13	20.19	18.75	16.84	18.62	20.15	15.84	17.64
Water activity (–)	–	–	–	–	–	–	–	–	–	0.833	0.846	0.550	0.545	0.857	0.861	0.823	0.838
Resin	(Control)																
Max fiber stress (kPa)	242.42	270.34	174.23	230.83	236.01	381.48	285.44	340.81	220.42	153.96	215.94	240.97	179.12	323.91	285.72	298.89	265.38
Modulus of elasticity (kPa)	1250.9	784.82	516.07	936.58	893.62	866.87	643.96	1250.15	1154.10	433.19	496.07	621.07	759.80	693.19	708.84	732.36	849.56
Color L (–)	63.83	35.91	34.86	60.71	56.89	53.82	59.31	72.53	74.69	35.13	38.58	38.55	44.37	35.22	36.94	51.66	56.42
Color a (–)	7.87	8.53	9.60	7.15	8.28	6.70	5.67	4.89	4.77	8.21	9.28	9.49	10.31	8.35	9.43	7.67	7.86
Color b (–)	15.17	13.81	14.00	18.34	17.50	16.27	13.05	14.64	12.44	14.73	17.11	17.95	20.41	15.33	17.28	19.95	20.33
Water activity (–)	0.796	0.900	0.904	0.850	0.828	0.919	0.924	0.905	0.914	0.803	0.807	0.697	0.674	0.832	0.841	0.828	0.817

somewhat moist and pliable. The data thus indicated that compression could be detrimental to the formation of strong wood glue composites, depending on the production process employed. In contrast, it appeared to aid the construction of a firmer matrix in the plastic resin glue samples.

Overall, heat treating the composites increased their average Modulus of Elasticity while decreasing their mechanical strength: the average stress was lowered from 177.79 kPa to 153.17 kPa, while the average Modulus of Elasticity increased from 433.48 kPa to 532.05 kPa. Again, however, the effects within adhesive categories were different. The resin glue composites tended to follow this same trend, but heating the wood glue samples increased the values appreciably in both parameters. In the resin glue trials, maximum allowable stress decreased by 37.78 kPa, or 14.5%, while Modulus of Elasticity increased by 156.81 kPa, for a 24.4% gain. In the glue composites, on the other hand, stress increased by 15.77 kPa, or 148.5%, while Modulus of Elasticity increased 35.6 kPa, or 242.3%. Heat treatment allowed the glue amalgam to dry more completely, thus forming a stronger final product. Therefore, from both a strength and durability standpoint, heat treatment appears to be essential if an adhesive based on glue is to be used. While heating resin amalgams increased stiffness, it did result in decreased strength, so the benefit of the treatment would need to be evaluated on a case-by-case basis, depending on the final product requirements.

The final factor studied was particle size. Once again, the behavior of the wood and resin glue adhesives were reverse. When particle size was decreased, there was a marked decrease in both maximum stress and Modulus of Elasticity in the glue trials, but a moderate increase in both for the resin glue trials. Wood glue stress decreased 15.65 kPa, or 52.8%, and the Modulus of Elasticity decreased 29.15 kPa, or 54.6% when particle size decreased. In the resin glue composites, on the other hand, switching from unground to ground DDGS (i.e., a decrease in particle size) increased the stress 20.3%, or 47.37 kPa, and the Modulus of Elasticity 4.9%, or 37.03 kPa. The resin glue results were expected, as there was more surface area for the formation of the matrix between adhesive and DDGS. Further research is needed to determine to what extent strength may be increased by decreasing particle size in resin glue composites. Other studies have noted that particle shape, size, surface properties, as well as distribution throughout the matrix affect the resulting mechanical properties of composites [15, 16].

The wood glue results do not follow this trend, though. One possible explanation may be that the glue used was considerably more viscous, and had a higher surface tension, which prevented it from infiltrating the smaller particles as thoroughly. However, further study would need to examine if this was indeed the cause. If it remained the case that larger particle sizes yielded stronger composites for glue-based adhesives, this behavior could aid cost-reduction during manufacturing, because a size reduction step would not be required.

The impetus behind this study was applicability for rapid prototyping, where high adhesive levels and low pressures are commonly used. As a first step toward that end, these results indicate that DDGS can be successfully used, but additional research is required if rapid prototyping applications are to be effectively implemented. Rapid prototyping processes are not as constrained as either injection or compression molding in terms of their ability to form complex three dimensional structures, as they rely on deposition processes, not mechanical compression [17–22].

Color

Color is an aspect that is often important for both aesthetic and structural reasons. Color change may indicate a compositional change in adhesive or DDGS, such as protein denaturization and degradation, or fat oxidation, both of which could have an adverse impact on composite performance. From a purely aesthetic standpoint, it is often desirable to have a final product that closely resembles the original constituents [7]. Moreover, color is an attribute that can be used to monitor product consistency.

On average, the resin glue composites retained a color closer to that of the original DDGS than did the glue composites (Tables 1, 3 and 4). For both adhesives, however, there was a moderate shift away from the yellow, and a slight decrease in the red cast. As brightness can be an important factor, resin glue, on the whole, yielded a more desirable finished product.

Quantity of DDGS had the largest total effect for both adhesives, but again, the effects were not entirely similar. For the resin glue treatments, brightness was increased substantially on addition of adhesive, while a slight decrease was observed in the glue composites. For both, a shift from yellow with increased adhesive was seen, although it occurred to a lesser extent in the glue. A movement away from the red was also observed in both, though in this instance the shift was greater for wood glue.

Heating caused a moderate increase in average brightness in the resin glue composites, but a moderate decrease in the glue samples. In both, a shift away from the golden brown hue of the DDGS was seen, although the wood glue retained more of the original color. Unfortunately, heat treatment is essential for wood glue composites, and consequently color may need to be sacrificed, at least to some degree, to achieve better product performance.

Compression did not have an effect on the color of the glue composites, aside from increasing the shift away from the red hues. There was, however, an increase in brightness and a larger decrease in redness observed in compressed resin glue samples than in uncompressed.

Interestingly, for both types of adhesives, although the original unground DDGS was darker than the ground DDGS, its final products were brighter. The reversal was likely caused by an interaction with the adhesive. There was a slight increase in red and yellow hues in unground DDGS samples in both adhesive categories.

If color were the main consideration in product design, resin amalgams would need less of the unground DDGS under compression at higher temperature, while wood glue products would require compression at ambient temperature and a higher percentage of unground DDGS. However, these treatment combinations were not ideal for mechanical strength, and so in some cases, other treatments to improve or alter color may need to be employed for these materials.

Water Activity

Water activity was also a crucial factor; it quantified the amount of unbound water available for use by microorganisms and chemical agents, and was therefore a measure of a material's susceptibility to deterioration and spoilage. Products with no free water ($a_W = 0.0$) are not at risk for spoilage, while materials that contain free water ($a_W = 1.0$) are at high risk for rapid spoilage. Materials have a reduced chance of bacterial growth below water activities of approximately 0.9, mold growth below approximately 0.7–0.8, and yeast growth below approximately 0.7 [23].

Temperature and compression greatly influenced water activity values. In the glue composites, heat treatment and lack of compression decreased the average water activity from 0.85 and 0.84, respectively, to 0.69, while in resin glue trials the decrease was from 0.87 to 0.81. When these treatments were combined, water activities as low as 0.55 for wood glue and 0.67 for resin glue were observed.

Increasing the DDGS content of resin glue samples decreased the water activity, on average. In both adhesives, particle size had no effect on water activity. The decrease in free water mirrored the increase in mechanical strength for wood glue composites, so these treatments would likely be quite useful in production. On average, resin glue composites had more unbound water, but because formaldehyde was present in the resin glue itself, preservatives, although helpful, would not be necessary.

Conclusions

Research was conducted to explore the fitness of DDGS as a biofiller in DDGS-based composites for rapid prototyping applications; the effects on the mechanical strength, color, and water activity were studied and evaluated. Resin glue proved to be far better suited to composite formation, yielding products that cured more uniformly, were stronger, and experienced less deterioration than those formed from glue. High DDGS content was essential for the formation of glue composites; a moderate amount of DDGS resulted in an increased maximum fiber stress, but decreased Modulus of Elasticity in the resin glue trials. Compression and decreased particle size were found to have a beneficial impact on both maximum fiber stress and Modulus of Elasticity, while heat treatment yielded mixed results. Although the treatments used did not produce high mechanical strength overall, some determinations can be made about their potential effectiveness. Future research is needed to determine what additional physical or chemical treatments could optimize adhesion, and thus mechanical strength, as well as decrease processing time, in these types of composites.

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